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(21) International Application Number: PCT/EP94/02670 (22) International Filing Date: 10 August 1994 (10.08.94) (30) Priority Data: 9316984.5 13 August 1993 (13.08.93) GB (71) Applicant (for AU BB CA GB IE KE LK MN MW NZ SD TT only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA GB IE KE LK MN MW NZ SD TT): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (72) Inventors: LYLE, Ian, Gardner; 60 Highland Avenue, Aston Park, Deeside, Clwyd CH5 1XQ (GB). ROSSER, David, Arthur; The Sycamores, The Mount, Heswall, Wirral, Merseyside L60 4RD (GB). (74) Agent: BRYANT, Tracey; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).	(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: CLEANSING COMPOSITION CONTAINING HYDROXY ALKANOATE DERIVATIVES		
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $R^1 \left[O - \underset{\substack{ \\ R^2}}{CH} - \overset{\substack{O \\ }}{C} \right]_p OR^3 \quad (I)$ </div> <div style="text-align: center;"> $C_xH_y - \overset{\substack{O \\ }}{C} - \quad (a)$ </div> </div>		
(57) Abstract <p>A skin cleansing composition for topical application to the human skin to remove make-up is an oil-in-water emulsion, containing an emulsifier system which comprises a hydroxy alkanooate derivative compound of general formula (I), wherein R¹ is H- or (a), R² is H- or C_pH_q- preferably CH₃, R³ is H-, C_xH_y-, or a metallic, ammonium, or alkylammonium cation, p is from 1 to 18, q is from 3 to 37, x is from 2 to 20, y is from 3 to 43, and m is from 1 to 3, provided that when R¹ is H-, then R³ is C_xH_y-, and when R¹ is C_xH_yCO-, then R³ is H-, or a metallic, ammonium or alkylammonium cation.</p>		

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Cleansing composition containing hydroxy alkanoate derivatives.

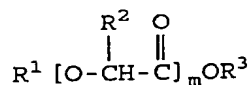
5 This invention relates to cleansing compositions. In particular, it relates to emulsion compositions of the oil-in-water type, which provide suitable wipe-off or rinse-off make-up removing and skin cleansing compositions.

10 Emulsion type make-up removing compositions, containing oil, water and a surfactant, are known. However, conventional compositions provide a less than satisfactory performance, in terms of either their ability to remove make-up, or their aesthetic and sensory properties. In
15 the case of oil based formulations, whilst these usually provide satisfactory make-up removal, they usually leave the user with a greasy afterfeel on the skin. With aqueous based products, there is a tendency for these to leave the skin feeling dry and tight after use.

20 The compositions of the current invention aim to remedy one or more of the deficiencies of the known compositions. In particular, it is an object of the invention to provide cleansing compositions which provide good cleansing and
25 afterfeel properties. Preferably these will also confer to the skin a long term moisturising benefit.

Thus, according to the invention, there is provided a cleansing composition suitable for topical application to
30 the human skin, comprising an oil-in-water emulsion system which comprises a hydroxy alkanoate derivative compound having the following general formula:

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wherein R^1 is H- or $C_xH_y-C(=O)-$
 R^2 is H- or C_pH_q-
 R^3 is H-, C_xH_y- , or a metallic, ammonium, or
 10 alkylammonium cation,
 p is an integer from 1 to 18
 q is an integer from 3 to 37
 x is an integer from 2 to 22,
 15 y is an integer from 3 to 43, and
 m is an integer from 1 to 3,

provided that when R^1 is H-, then R^3 is C_xH_y- , and when R^1
 is C_xH_yCO- then R^3 is H-, or a metallic, ammonium or
 20 alkylammonium cation.

The invention also provides a method of removing make up
 from skin by applying a composition as above to the skin,
 and then wiping, washing or rinsing the emulsion from the
 25 skin.

The hydroxy alkanoate derivative above will generally
 function as an emulsifier which is part of all of an
 emulsifier system. However, it may be included as at
 30 least part of the oil of the emulsion - this applies
 particularly to lipophilic alkyl esters of hydroxy
 alkanolic acids, (in which compounds, R^1 above is H)

The hydroxy alkanoate derivatives employed in compositions
 according to the invention provide the cleansing
 35 composition with desirable properties, in the sense that
 they may not only act as an emulsifier within the
 composition, thereby stabilising the oil-in-water

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emulsion, but can also be beneficially metabolised in the skin.

5 During this process, naturally occurring enzymes in the skin cleave the hydroxy alkanoate derivative in the composition to generate lactic acid or glycolic acid (depending on whether R^2 is H or CH_3 - in the above general formula), which may then permeate further through the skin. In particular, it is thought that the derivatives
10 described penetrate the skin more readily than glycolic or lactic acids themselves, which are relatively hydrophilic.

Absorption of lactic acid, glycolic acid or other hydroxy alkanoic acid into the skin is desirable, because these
15 compounds have a humectant action, they provide a moisturisation benefit, and they also improve the condition and feel of skin.

It has also been found to be a highly desirable aspect of
20 the invention that the hydroxy alkanoate derivative used in compositions according to the invention has an hydrophilic/lipophilic balance (HLB) value of less than about 5.5. It is suspected that hydroxy alkanoate derivatives with this range of HLB values may more readily
25 partition into the skin, and hence deliver a cosmetic benefit more deeply in the skin, because of their hydrophobicity.

In the formula given above R^2 is preferably H or CH_3 , more
30 preferably CH_3 , so that the compound is a derivative of glycolic or lactic acid.

Lactic acid derivatives are readily available commercially, and preferred for this reason. However,
35 homologues of the lactic derivatives are accessible and can also be used.

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Acyl derivatives of 2-hydroxy alkanate acids in which R^2 is C_pH_q - and p is 2 or more can be made by reaction of an acyl halide with the 2-hydroxy alkanate acid. Alkyl esters of 2-hydroxy alkanate acids can be prepared by
5 esterification of those acids.

If R^2 is C_pH_q - and p is 2 or more, then p is preferably in the range 2 to 12, more preferably 2 to 6.

10 According to one preferred aspect of the invention, the hydroxy alkanate derivative in the cleansing composition is an acyl lactate; that is, in the general structure shown above, R^3 is H-, R^2 is CH_3 and R^1 is C_xH_yCO- . In a particularly preferred variant of acyl lactates, in R^1 x
15 is between 14 and 20, and is most preferably 17.

In a further preferred variant of acyl lactates, the R^3 species is a metallic cation which provides a relatively insoluble acyl lactate species, such as a calcium or magnesium cation. A most preferred embodiment of the
20 invention comprises calcium stearoyl lactate, which has an HLB value of 5.1. Using such a relatively insoluble acyl lactate may provide particularly beneficial properties to the composition.

25 Acyl lactates are anionic surfactants, and are conveniently prepared by coupling lactic acid to long chain fatty acids via the alpha hydroxy group on the lactic acid. Such acyl lactates surfactants are believed to readily break down in the skin to provide
30 lactic acid, thereby providing the aforementioned beneficial absorption of lactic acid into the skin.

Another preferred category of hydroxy alkanate derivatives for use in cleansing compositions according to
35 the invention are alkyl lactates; that is R^1 is H- and R^2 is CH_3 , and R^3 is C_xH_y . In a more preferred embodiment, x

- 5 -

in R^3 is between 6 and 20, more preferably 12 and 18. In the most preferred embodiment, R^3 is 14.

Alkyl lactates are weak nonionic surfactants, in which the lactic acid moiety is linked to a long chain fatty alcohol through its carboxylate group. Alkyl lactates surfactants are essentially water insoluble, and therefore may provide a relatively poor foaming ability when compared to acyl lactylate surfactants, but may beneficially be used in compositions according to the invention, because of their ability to partition into the skin. This ability is often superior to that of the anionic acyl lactylate surfactants.

It is a characteristic of certain preferred embodiments of the invention that they may provide compositions which are relatively stable in use, thereby providing compositions which are commercially more attractive. By stable it is meant that the emulsion does not visibly breakdown to its constituent phases within one month of being prepared, in temperate conditions.

A preferred alkyl lactate for use in compositions according to the invention is myristyl lactate. This alkyl lactate has a very low HLB value, in the region 1-3.

The concentration of the hydroxy alkanoate derivative of the general structure above in the composition is typically 0.5-10% by weight of the composition. However, the hydroxy alkanoate derivative of the general formula discussed is typically only one emulsifier which may be part of an emulsifier system used in compositions according to the invention. If used, such other emulsifiers may be used to make the total level of emulsifier system in compositions according to the invention to be between 0.5-10% by weight, more preferably 1-7% by weight.

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Such other emulsifiers as may be used in the emulsifier system according to the invention may include any emulsifier or combination of emulsifiers which has an average HLB value of greater than 6, more preferably greater than 9, and may be readily selected from any textbook on the subject.

The oil phase of compositions according to the invention may comprise mineral oils, hydrocarbons, silicone oils, triglyceride/ester oils, or mixtures thereof. Preferred oils are those which are particularly effective at solubilising the oil components of make up. Particularly preferred oils for use in compositions according to the invention are hydrocarbon oils, such as isoparaffins, polydecene and polybutene, mineral oils and esters which contain a saturated or unsaturated, straight or branched chain C₈₋₂₂ alkyl or alkenyl group, for example isopropylmyristate, hexyl laurate, methyl laurate, 2-ethylhexyl palmitate, 2-octadecyl myristate, isopropylpalmitate, and triglycerides such as glyceryl tricaprylate/caprate (eg ESTOL, ex. Unichema), glyceryl tri-isostearate (eg PRISORINE, ex. Unichema), and glyceryl tri- (2-ethylhexanoate) (eg MYRITOL GTEH, ex. Henkel).

Preferably, the composition comprises a hydrocarbon oil, or a hydrocarbon oil in combination with an ester oil as described above.

Particularly preferred oils for use in compositions according to the invention are isoparaffin and polydecene. These components are preferred components in the oil phase, since they are particularly effective in blending into and lifting a certain resilient make-up compositions which are typically resistant to removal, such as for example water-proof eye make-ups.

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Preferably, the oil is present in the composition at a level of 3-60%, more preferably 10-40% by weight of the composition.

- 5 The water in compositions according to the invention may preferably comprise from 95-40%, more preferably 90-50% by weight of the composition.

10 The composition according to the invention may additionally comprise further adjuncts as are typically found in such cleansing compositions. These may typically include;

- thickeners, such as carbomers, xanthan gum, hectorite, and fumed silica,
- 15 - humectants, such as glycerol, propylene glycol, dipropylene glycol, sorbitol, and 2-pyrrolidone-5-carboxylate,
- perfumes,
- colourants,
- 20 - preservatives, such as salicylic acid, p-hydroxybenzoate esters, and 2-bromo-2-nitropropane-1,3-diol,
- antioxidants, such as butylated hydroxy toluene, tocopherol, and butylated hydroxy anisole,
- 25 - short-chain monohydric alcohols, such as ethanol and isopropanol,
- skin conditioners, such as polyquaternium 10 and PEG-7 glyceryl cocoate,
- germicides, such as triclosan and cetrimide, and
- 30 - plant extracts, such as aloe vera, cornflower, witch hazel, elderflower, and cucumber.

Products according to the invention may take any convenient product form, and as such may be in the form of
35 lotions, creams, or may be readily combined in known ways with a suitable propellant to provide a product in mousse form.

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Examples

The invention will now be demonstrated with reference to the following example:

5

Composition (%w/w)

<u>Component</u>	<u>1</u>	<u>2</u>
Ethylflo 362 NF (1)	20.0	20.0
Permethyl 101A (2)	10.0	10.0
10 Cremophor RH40 (3)	2.0	-
Cremophor A6 (4)	-	2.00
Renex 30 (5)	0.30	0.30
Alfol 1618 (6)	3.00	3.00
Crodamol ML (7)	3.00	-
15 Crolactil CSL (8)	-	5.00
Nipasol M (9)	0.10	0.10
Nipagin M (10)	0.20	0.20
Carbopol 980 (11)	0.30	0.30
Triethanolamine	0.40	1.36
20 Water	60.70	57.74

(pH 6.6) (pH 5.9)

- (1) Polydecene dimer, ex. Ethyl Co.
- 25 (2) Isohexadecane, ex. Waren Empfänger
- (3) PEG-40 hydrogenated castor oil, ex. BASF
- (4) Ceteareth-6 and Stearyl alcohol, ex. BASF
- (5) Trideceth-12, ex. ICI
- (6) Cetearyl alcohol, ex. Condea
- 30 (7) Myristyl lactate, ex. Croda
- (8) Calcium stearoyl lactylate ex. Croda
- (9) Propyl paraben, ex. Nipa Labs.
- (10) Methyl paraben, ex. Nipa Labs.
- (11) Carbomer, ex. Goodrich

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Compositions 1 and 2 were prepared by blending together the components of the composition as shown.

Preparation method

5

Compositions 1 and 2 were prepared according to the following general method.

10 Firstly the aqueous phase is prepared by blending the Nipagin and triethanolamine with an aliquot of water, and heating the mixture to 70-80°C. The oil phase is then prepared by adding the Ethylflo 362 NF, Permethyl 101A, Cremophor RH40, Renex 30, Alfol 1618, Nipasol, and the hydroxy alkanoate derivative to a container and heating to
15 70-80°C. The oil phase is then blended into the aqueous phase using a Silverson mixer.

20 Into this is blended the polymeric thickener, which is pre-prepared by adding the Carbopol gradually, with stirring, into the remaining water, and subsequently heating this to 70-80°C.

The composition is finally adjusted to pH 6-6.6 using triethanolamine, where necessary.

25

Compositions 1 & 2 were evaluated for their make-up removal efficacy against a commercially available product, and were also tested for the deposition of lactic acid that occurred after use on human skin.

30

Make-up Removal Efficacy

35 Compositions 1 and 2 were assessed for their make-up removal efficacy, against the commercially available product Oil of Ulay Water Rinsable Cold Cream. This product contains water, mineral oil, polyalphaolefin, glycerin, isododecane, sorbitan stearate, cyclomethicone,

- 10 -

caprylic/capric triglyceride, hexylene glycol, PEG-8 laurate, stearyl alcohol, Ceteareth-20, lauryl glycoside, acrylic acid copolymer, castor oil, cetyl alcohol, dioctyl sodium sulphosuccinate, methylchloroisothiazolinone and
5 methylisothiazolinone, PEG-10 soya sterol, triethanolamine, and fragrance.

Test Protocol

- 10 Approximately 0.015g of Shiseido Waterproof Eyeliner is then applied to three 3cmx2cm designated patches on a tester's forearm. Prior to application, the colour of the skin is measured using a Minolta Chroma Meter CR-100, to give a set of baseline readings (A). The 3-D colour co-
15 ordinate system L*a*b was used, and each recorded result was the average of 6 individual measurements. A panel of 9 people were used. After application and drying, a second colour measurement was taken (B)
- 20 To this is applied 0.2 g of the cleansing composition being tested, the composition being gently rubbed into the test area with either 40 or 100 light circular rubbing motions. The composition is subsequently removed either by wiping off with a tissue in two motions, forward and
25 back, or rinsing with water at flow rate of approx. 6 l/min, and a temperature of approximately 35°C. All patches are dried, and final colour measurements are taken (reading C).
- 30 The percentage removal is calculated as $(B-C)/(B-A) \times 100$, where B-A is the difference in L, a, and b readings, and so on for B-C.

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Results

% make-up removal

Composition	40 rubs/wipe off	100 rubs/rinse off
1	46.9%	43.4%
2	58.0%	65.6%
Oil of Ulay Water Rinsable Cold Cream	40.0%	37.1%

- As can be seen from the above results, compositions 1 and 2 provided superior make-up removal efficacy to the commercially available formulations under both test protocols, and may also deliver to the skin a longer term skin benefit, due to absorption by the skin of the hydroxy alkanoate derivative.

Example 2

- The following composition provides a cleansing milk composition.

<u>Component</u>	<u>% (w/w)</u>
Cetearyl alcohol (Alfol1618, ex. Condea)	2.0
Trioctanoin (Estol3609, ex. Unichema)	5.0
Polydecene (Ethylflo 362NF, ex. Ethyl)	5.0
Calcium stearoyl lactylate (Crolactil CSL, ex Croda)	1.0
Ceteth 21 (Brij 721, ex. ICI)	3.0
Ceteth 2 (Brij 72, ex. ICI)	1.0
Propyl Paraben (Nipasol, ex. Nipa)	0.2
Glycerine (ex. Unichema)	2.0
Methyl Paraben (Nipagin M, ex. Nipa)	0.2
Xanthan gum (Kelzan, ex. Kelco)	0.1
Perfume	q.v
Water	to 100

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Example 4

The following composition provides a cleansing lotion according to the invention.

5		
	<u>Component</u>	<u>% (w/w)</u>
	C ₁₁ -C ₁₃ isoparaffin (Isopar L, ex. Exxon)	5.0
	Caprylic/capric triglyceride (Miglyol 810,	
10	ex.Huls)	15.0
	Myristyl lactate (Crodamol ML, ex. Croda)	2.0
	Cetearyl alcohol (Alfol 1618, ex. Condea)	3.0
	Ceteth 21 (Brij 721, ex. ICI)	1.0
	Propyl paraben (Nipasol M, ex. Nipa)	0.1
15	Propylene glycol (ex. BASF)	3.0
	Triethanolamine (ex. BASF)	0.2
	Carbomer 934 (Carbopol 934, ex. Goodrich)	0.2
	Methyl paraben (Nipagin M, ex. Nipa)	0.2
	DMDM hydantoin (Glydant, ex. Lonza)	0.2
20	Perfume	q.v
	Water	to 100

Example 5

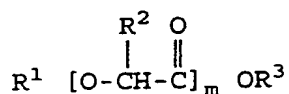
25 The following composition provides an aerosol cleansing mousse composition according to the invention.

	<u>Component</u>	<u>% (w/w)</u>
30	Isopropyl myristate (Estol 1514, ex. Unichema)	25.0
	PEG-8 laurate (Clihrol 4ML, ex. Croda)	6.0
	Myristyl lactate (Crodamol ML, ex. Croda)	2.0
	Glycerine (ex. Unichema)	2.0
	Butane (Cap 30, ex. Calor)	5.0
35	Water	to 100

CLAIMS

- 5 1. A skin cleansing composition for topical application to the human skin to remove make up therefrom comprising an oil-in-water emulsion containing a hydroxy alkanoate derivative compound of the following general formula:

10



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wherein R^1 is H- or $C_xH_y-C(=O)-$
 R^2 is H- or C_pH_q-
 R^3 is H-, C_xH_y- , or a metallic, ammonium, or
 20 alkylammonium cation,
 p is an integer from 1 to 18,
 q is an integer from 3 to 37,
 x is an integer from 2 to 20,
 y is an integer from 1 to 3,

25

provided that when R^1 is H-, then R^3 is C_xH_y- , and
 when R^1 is C_xH_yCO- , then R^3 is H-, or a metallic,
 ammonium or alkylammonium cation.

- 30 2. A cleansing composition according to claim 1 wherein R^2 is H or CH_3 .
3. A cleansing composition according to claim 1 or claim 2, wherein the hydroxyalkanoate derivative has an HLB
 35 value of less than 5.5.
4. A cleansing composition according to any one of the preceding claims, wherein the oil phase comprises a mineral oil, a hydrocarbon oil, or an ester which

contains a saturated or unsaturated straight or branched C₈-C₂₂ alkyl or alkenyl chain, or mixture thereof.

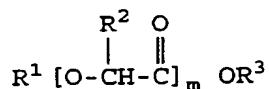
- 5 5. A cleansing composition according to any one of the preceding claims wherein the amount of oil in the oil phase of the emulsion is 3 to 60% by weight of the composition and the amount of the hydroxy alkanoate derivative is 0.5 to 7% by weight of the composition.

10

6. A method of removing cosmetics from human skin, comprising:

- (i) applying to skin with make up thereon a skin cleansing composition which has an oil-in-water emulsion containing a hydroxy alkanoate derivative compound of the following general formula:

20



25

wherein R^1 is H- or $C_xH_y-\overset{\overset{O}{||}}{C}-$
 R^2 is H- or CH₃
 R^3 is H-, C_xH_y-, or a metallic, ammonium, or alkylammonium cation,
 p is an integer from 1 to 18,
 q is an integer from 3 to 37,
 x is an integer from 2 to 20,
 y is an integer from 1 to 3,

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provided that when R^1 is H-, then R^3 is C_xH_y-, and
 when R^1 is C_xH_yCO-, then R^3 is H-, or a metallic, ammonium or alkylammonium cation, and

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(ii) wiping, washing or rinsing said emulsion from the skin.

7. A method according to claim 6 wherein R^2 is H or CH_3 .
8. A method according to claim 6 or claim 7, wherein the hydroxyalkanoate derivative has an HLB value of less than 5.5.
9. A method according to any one of claims 6 to 8, wherein the oil phase comprises a mineral oil, a hydrocarbon oil, or esters which contain a saturated or unsaturated straight or branched chain C_8 - C_{22} alkyl or alkenyl group, or mixtures thereof.
10. A method according to any one of claims 6 to 9 wherein the amount of the oil is 3 to 60% by weight of the emulsion and the amount of the hydroxyalkanoate derivative is 0.5 to 7% by weight of the emulsion.
11. Use of a hydroxyalkanoate derivative as defined in any one of claims 1 to 3 as an emulsifier in a composition for removing make up from human skin.

INTERNATIONAL SEARCH REPORT

Int. l. Application No
PCT/EP 94/02670

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/02 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 541 347 (UNILEVER) 12 May 1993 -----	
A	EP,A,0 150 914 (UNILEVER) 7 August 1985 -----	

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